

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-319398

(43)Date of publication of application : 31.10.2002

(51)Int.Cl.

H01M 4/58

H01M 4/02

H01M 10/40

(21)Application number : 2001-122449

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(22)Date of filing : 20.04.2001

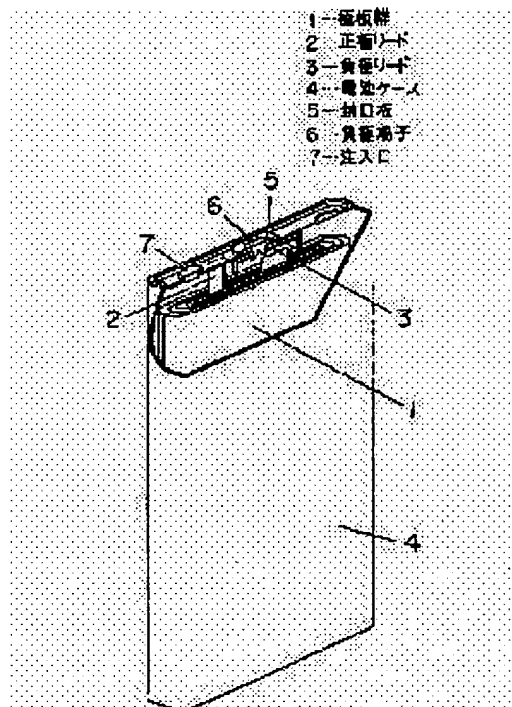
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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To heighten a discharge capacity, and to make a low temperature characteristic, a cycle characteristic, an overdischarge restoration characteristic and thermal stability in an overcharge time enhanced compatibly.

SOLUTION: A positive active material for a nonaqueous electrolyte secondary battery comprising a positive electrode mixed with $\text{Li}_x\text{Co}_y\text{M}_z\text{W}_w\text{O}_z$ ($1.10 \geq x \geq 0.9$, $0.98 \geq y \geq 0.85$, $0.02 \leq w \leq 0.15$, $z=1.8-2.2$, M is at least one kind or more of element selected from the group comprising Al, Cu, Zn, Mg, Ca, Ba and Sr) as the first positive active material, and LiANiBM'COD ($1.02 \geq A \geq 0.3$, $0.98 \geq B \geq 0.5$, $0.02 \leq C \leq 0.5$, $D=1.8-2.2$, M' is at least one kind or more of element selected from the group comprising Co, Mn, Cr, Fe, V and Al as the second positive active material is used.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The negative electrode which can emit [occlusion and] a lithium, and the nonaqueous electrolyte of lithium ion conductivity, As a separator or a lithium ion conductivity layer, and the first active material of a positive electrode, $\text{Li}_x\text{Co}_y\text{M}_w\text{O}_z$, $1.10 \geq x \geq 0.9$, $0.98 \geq y \geq 0.85$, $0.02 \leq w \leq 0.15$, and $z = 1.8-2.2$ At least one or more kinds of elements chosen from aluminum, Cu, Zn, Mg, calcium, Ba, and Sr, It is LiANiBM'COD (it Co(es) $1.02 \geq A \geq 0.3$, $0.98 \geq B \geq 0.5$, $0.02 \leq C \leq 0.5$, $D = 1.8-2.2$, and M') as the second active material of a positive electrode. The nonaqueous electrolyte rechargeable battery using the positive electrode which mixed at least one or more kinds of elements chosen from Mn, Cr, Fe, V, and aluminum.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by the range of the mixing ratio of the first above-mentioned active material of a positive electrode and the second active material of a positive electrode being 95:5-30:70 in a weight ratio.

[Claim 3] The negative electrode which can emit [occlusion and] a lithium, and the nonaqueous electrolyte of lithium ion conductivity, As a separator or a lithium ion conductivity layer, and the first active material of a positive electrode (Li1-RMR), $\alpha(\text{Co1-SMS})$ βOgamma (However, $0.02 \leq R+S \leq 0.15$, $\alpha/\beta = 0.90-1.10$, $\gamma = 1.8-2.2$, and one sort as which the alloying element M was chosen from aluminum, Cu, Zn, Mg, calcium, Ba, and Sr), It is LiANiBM'COD (it Co(es) $1.02 \geq A \geq 0.3$, $0.98 \geq B \geq 0.5$, $0.02 \leq C \leq 0.5$, $D = 1.8-2.2$, and M') as the second active material of a positive electrode. The nonaqueous electrolyte rechargeable battery using the positive electrode which mixed at least one or more kinds of elements chosen from Mn, Cr, Fe, V, and aluminum.

[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by the range of the mixing ratio of the first above-mentioned active material of a positive electrode and the second active material of a positive electrode being 95:5-30:70 in a weight ratio.

[Claim 5] The nonaqueous electrolyte rechargeable battery according to claim 1 to 4 whose mean particle diameter of the first above-mentioned active material of a positive electrode is 5 micrometers to 20 micrometers.

[Claim 6] The nonaqueous electrolyte rechargeable battery according to claim 1 to 5 whose specific surface area of the first above-mentioned active material of a positive electrode is $1.2\text{m}^2/\text{g}$ from $0.3\text{m}^2/\text{g}$.

[Claim 7] The nonaqueous electrolyte rechargeable battery according to claim 1 to 6 whose mean particle diameter of the second above-mentioned active material of a positive electrode is 2 micrometers to 20 micrometers.

[Claim 8] The nonaqueous electrolyte rechargeable battery according to claim 1 to 7 whose specific surface area of the second above-mentioned active material of a positive electrode is $1.5\text{m}^2/\text{g}$ from $0.3\text{m}^2/\text{g}$.

[Claim 9] The cell system using a nonaqueous electrolyte rechargeable battery without an overdischarge prevention circuit according to claim 1 to 8.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] The technical field to which this invention belongs is related with the cell system containing the nonaqueous electrolyte rechargeable battery used for a Personal Digital Assistant, pocket electronic equipment, home small stationary-energy-storage equipment, the motor bicycle that makes a motor the source of power, an electric vehicle, a hybrid electric vehicle, etc., its cell, and a peripheral device.

[0002]

[Description of the Prior Art] In recent years, the nonaqueous electrolyte rechargeable battery used as a main power supply of mobile communication equipment and pocket electronic equipment has high electromotive force, and has the features which are high energy consistencies. As positive active material used here, there are a cobalt acid lithium (LiCoO_2), a nickel acid lithium (LiNiO_2), etc. These active materials have the electrical potential difference beyond 4V to the lithium.

[0003] Although the charge-and-discharge capacity of a lithium compound nickel oxide is large among these positive active material, in order that a crystal lattice might repeat expansion contraction by performing charge and discharge, the lattice strain, the crack of structure destruction and a particle, etc. occurred, and the fall of the discharge capacity accompanying a charge-and-discharge cycle was produced. (S. Yamada, M. Fujiwara and M. Kanda, J. Power Source, 54,209 (1995)) In the condition that Li ****ed in the charge condition, when the crystal structure is unstable and the cell was heated in this condition, there was a problem to which positive active material falls the safety of a lifting cell in a pyrolysis reaction again. Then, in order to solve this technical problem, by permuting some nickel by other elements, stabilization of a crystal lattice was attained and the report which makes an improvement of a cycle property and safety has been made. (For example, $\text{Li}_y\text{Ni}_x\text{Co}_{1-x}\text{O}_2$: JP,63-299056,A, $\text{Li}_x\text{MyNzO}_2$ (however, M was chosen from Fe, Co, and nickel it is kind at least and N was chosen from Ti, V, Cr, and Mn at least kind): JP,4-267053,A) etc. -- it is proposed.

[0004] If other elements permute some nickel of a lithium compound nickel oxide as mentioned above, charge-and-discharge capacity becomes large, and since there are few amounts of surplus lithiums given to a negative electrode in the state of overcharge, high safety is maintainable at the time of overcharge. The discharge engine performance deteriorates remarkably from the diffusion in the crystal lattice of the lithium ion in ** and low temperature being slow. Furthermore, the capacity difference (irreversible capacity) of the first time charge after a cell configuration and discharge is large, since cell capacity becomes positive-electrode regulation, when a cell is put on an overdischarge condition, positive-electrode potential descends to about 0V, and there is a problem that the recovery property of a cell deteriorates remarkably by reduction disassembly of positive active material. The lithium compound nickel oxide which permuted some nickel by other elements for this problem is set in the commercial scene, and has not spread yet.

[0005] Moreover, although the method of, establishing the electrical circuit which prevents overdischarge in the outside of a cell by current on the other hand, and preventing the overdischarge

itself is used, when the electrical circuit which prevents overdischarge exists, there is a problem to which costs, such as a device which uses a cell, or a cell pack, become high.

[0006] In this fuel cell subsystem, if it discharges until cell voltage is set to 0V, since the irreversible capacity of a positive electrode is smaller than the irreversible capacity of a negative electrode, it will become negative-electrode capacity regulation, the potential of a negative electrode will become more than the dissolved potential (3V neighborhood) of the copper used for the charge collector, or nickel, and copper and nickel will dissolve into the electrolytic solution. And when a cell was charged again, in order for these metallic compounds to deposit and to check the charge-and-discharge reaction of a lithium on a negative-electrode active material, there was a problem on which a cell property deteriorates. In order to prevent this, the approach (JP,3030996,B) it is made for the potential of a negative electrode not to go up to the dissolved potential of copper or nickel even if cell voltage is set to 0V is reported by by sticking a lithium metal on a negative electrode beforehand. Moreover, the approach of solving LiMnO₂ with a large irreversible capacity etc. by the approach (JP,07-288124,A) of adding to a positive electrode to a positive electrode is proposed.

[0007]

[Problem(s) to be Solved by the Invention] However, by the approach of sticking a metal lithium on a negative electrode, in case a cell is constituted, it is necessary to secure the volume for the metal lithium beforehand, and becomes the hindrance at the time of raising the volume energy density of a cell. Moreover, when LiMnO₂ is added to a positive electrode, as for irreversible capacity, LiMnO₂ is large, but compared with LiCoO₂, since there is little the reversible charge-and-discharge capacity, capacity falls to the cell used as the active material only by LiCoO₂ by adding LiMnO₂.

[0008] In order to solve such a problem, the nonaqueous rechargeable battery which contained Li_yNi_sCo_{1-s}MO₂ (y is a value at the time of cell assembly, and is $1.01 \leq y \leq 1.10$ and $0.65 \leq s \leq 0.90$) of a lithium compound nickel oxide which permuted some of Li_xCoO₂ (x is a value at the time of cell assembly, and is $1.01 \leq x \leq 1.10$) and above-mentioned nickel by other elements by JP,2000-340229,A and JP,2000-340228,A in the positive electrode is proposed.

[0009] However, even if it has effectiveness to overdischarge by mixing of Li_xCoO₂ as mentioned above, since it still has the half lithium in the crystal structure also in the charge condition (Li_{0.5}CoO₂), Li_xCoO₂ has left the technical problem which a superfluous lithium deposits and spoils the safety of a cell remarkably on a negative electrode, when this cell overcharges by a certain reason.

[0010]

[The means which invention tends to solve] In order to solve this technical problem, this invention mainly uses positive active material as the first active material. Li_xCo_yM_wO_z, $1.10 \geq x \geq 0.9$, $0.98 \geq y \geq 0.85$, $0.02 \leq w \leq 0.15$, and $z = 1.8-2.2$ M At least one or more kinds of elements chosen from aluminum, Cu, Zn, Mg, calcium, Ba, and Sr, It is LiANiBM'COD (it Co(es) $1.02 \geq A \geq 0.3$, $0.98 \geq B \geq 0.5$, $0.02 \leq C \leq 0.5$, $D = 1.8-2.2$, and M') as the second active material of a positive electrode. At least one or more kinds of elements chosen from Mn, Cr, Fe, V, and aluminum are mixed, and the fall of discharge capacity and an improvement of an overdischarge property are obtained.

[0011] It has the following effectiveness by including at least two kinds, the lithium compound nickel oxide which introduced the different-species element as positive active material as mentioned above, and the lithium compound cobalt oxide which introduced the different-species element.

[0012] 1) By introducing a different-species element into two kinds of each active material, were improved with each active material or the above-mentioned effectiveness that 3 charge-and-discharge capacity which is excellent in 2 overcharge safety which is excellent in an overdischarge property is high is the property of a proper at each active material.

[0013] Furthermore, it has the following synergistic effects by mixing two kinds. That is, while safety of the lithium compound cobalt oxide which introduced the different-species element improves, since the introduced element oxidizes and it is eluted, it has the demerit that the preservation property in an elevated temperature falls. By the invention in this application, the above-mentioned oxidation reaction is cancelable to it by mixing the lithium compound nickel oxide which introduced the different-species element with the electronic automatic exchange of lithium compound cobalt oxide and a lithium

compound nickel oxide. That is, it excels in a preservation property as the 4th effectiveness.

[0014] Furthermore, it is still more effective that the different-species element to introduce permutes a part of both of some lithiums of positive active material, nickel, or cobalt. This is because distortion of the crystal structure by charge and discharge is canceled and a cycle property improves that the thermal stability in a overcharge condition improves, and by going into a transition-metals layer, when a different-species element goes into a lithium layer.

[0015]

[Embodiment of the Invention] the empirical formula $\text{Li}_x\text{Co}_y\text{M}_w\text{O}_z$ of the first active material of a positive electrode of this invention ($1.10 > x > 0.9$, $0.98 > y > 0.85$, $0.02 \leq w \leq 0.15$, and $z = 1.8 - 2.2$) In at least one or more kinds of elements chosen from aluminum, Cu, Zn, Mg, calcium, Ba, and Sr, although structure stabilization of a positive electrode improves further when the addition of an alloying element M is made or more into 0.15, the fault that the fall of cell capacity becomes large is produced. Moreover, sufficient effectiveness of structure stabilization is not acquired less than by 0.02. It is necessary to set the addition of an alloying element M to $0.02 \leq w \leq 0.15$ from this.

[0016] Cycle degradation it is considered to be as a cause that the amount out of a positive electrode of generation of gas increased when mean particle diameter of said first active material of a positive electrode is set to 5 micrometers or less arose, and also when referred to as 20 micrometers or more, the technical problem to which a heavy load property and cell capacity fall arose. As for this to mean particle diameter, it is desirable to be referred to as 5-20 micrometers.

[0017] Moreover, when specific surface area was similarly made below into $0.3 \text{ m}^2/\text{g}$, a heavy load property and cell capacity fell, and when it carried out more than $1.2 \text{ m}^2/\text{g}$, cycle degradation it is considered to be as a cause that the amount out of a positive electrode of generation of gas increased arose. As for this to specific surface area, it is desirable to be referred to as $0.3 - 1.2 \text{ m}^2/\text{g}$.

[0018] Second active material $\text{LiANiBM}'\text{COD}$ of a positive electrode of this invention (it Co(es) $1.02 \geq A \geq 0.3$, $0.98 \geq B \geq 0.5$, $0.02 \leq C \leq 0.5$, $D = 1.8 - 2.2$, and M') In at least one or more kinds of elements chosen from Mn, Cr, Fe, V, and aluminum, although structure stabilization of a positive electrode improves further when the addition of alloying element M' is made or more into 0.5, the technical problem that the fall of the cell capacity which is the description of a lithium nickel oxide becomes large arises. Moreover, structure stabilization is not obtained less than by 0.02. It is necessary to set the addition of alloying element M' to $0.02 \geq C \geq 0.5$ from this.

[0019] Cycle degradation it is considered to be as a cause that the amount out of a positive electrode of generation of gas increased when mean particle diameter of the second active material of a positive electrode of this invention is set to 2 micrometers or less arose, and also when referred to as 20 micrometers or more, the technical problem to which a heavy load property and cell capacity fall arose. As for this to mean particle diameter, it is desirable to be referred to as 2-20 micrometers.

[0020] Moreover, when specific surface area was similarly made below into $0.3 \text{ m}^2/\text{g}$, a heavy load property and cell capacity fell, and when it carried out more than $1.5 \text{ m}^2/\text{g}$, cycle degradation it is considered to be as a cause that the amount out of a positive electrode of generation of gas increased arose. As for this to specific surface area, it is desirable to be referred to as $0.3 - 1.5 \text{ m}^2/\text{g}$.

[0021] If heating composition is carried out at an elevated temperature, since reversible charge-and-discharge capacity will fall, said second active material of a positive electrode has that most effective by which heating composition was carried out in the 750 to 1000 degrees C temperature requirement.

[0022] As for the first active material of a positive electrode, and the second active material of a positive electrode, it is desirable to mix in 95:5-30:70 by the weight ratio. When there are few second active materials of a positive electrode than 5%, the recovery property after overdischarge is a little inferior, and when there are more second active materials of a positive electrode than 70%, a low-temperature property is a little inferior.

[0023] The first active material of a positive electrode and the second active material of a positive electrode of claim 1 of this invention are obtained by mixing and calcinating so that it may become the mole ratio of the active material of a request of the raw material of lithium salt, cobalt, or nickel, and the raw material containing an alloying element M or M' .

[0024] In order to compound the first active material of a positive electrode of claim 3 of this invention, a cobalt raw material and the raw material containing an alloying element M are first dissolved into a water solution. At this time, these raw materials have a desirable sulfate. An alkali water solution is dropped continuously, controlling pH of a solution in this mixed solution, and the hydroxide (this is hereafter called a precursor.) which is a coprecipitate of cobalt and an alloying element M is compounded. Furthermore, it is obtained by mixing and calcinating the raw material containing this precursor, a lithium raw material, and an alloying element M.

[0025] It is based on the following reasons that the positive active material compounded here has the target structure. By the mole ratio of each element added in the first place at the time of composition, the cobalt and the alloying element M in the hydroxide compounded as a precursor should occupy a hydroxyl group and all 6 coordination locations to configure. In case this precursor is used for the second and positive active material is compounded, it is mixing and compounding so that the lithium and alloying element M in the lithium raw material which mixes the lithium location of LiCoO_2 may occupy all. The active material compounded by such approach is expressed by $\alpha(\text{Co1-SMS})\beta\text{O}\gamma$ (however, $0.02 \leq R+S \leq 0.15$, $\alpha/\beta = 0.90-1.10$, $\gamma = 1.8-2.2$, one sort as which the alloying element M was chosen from aluminum, Cu, Zn, Mg, calcium, Ba, and Sr) by the strict analysis by the X diffraction (Li1-RMR).

[0026] Since in other words the total of the number of mols of a lithium and an alloying element M mixed behind is the same as the total of the number of mols of cobalt and an alloying element M contained in the precursor, the alloying element M added to behind will be permuted by the lithium location which is an empty shell in the crystal structure of the compound positive active material. This is understood also from the structural optimization in the crystal structure analysis of the obtained positive active material.

[0027] The bonding strength of the layer which consists of the metal oxide layer and alloying element M which consist of an alloying element M and cobalt, and a lithium by the above is made to strengthen, and positive active material with higher thermal stability can be offered in a overcharge condition.

[0028] Moreover, the lithium nickel oxide produced by the first active material of a positive electrode of above-mentioned claim 3 and the same approach can be used for the second active material of a positive electrode. In that case, as mentioned above, when a different-species element goes into a lithium layer, that the thermal stability in a overcharge condition improves, and by going into a transition-metals layer, distortion of the crystal structure by charge and discharge is canceled, and the effectiveness that a cycle property improves is acquired like the first active material of a positive electrode.

[0029] The target nonaqueous electrolyte rechargeable battery is obtained by these two kinds of active materials by adjusting a mixing ratio, mixing and constituting a positive electrode (the mixing ratio of the first above-mentioned active material of a positive electrode and the second active material of a positive electrode being specifically the range of 95:5-30:70 at a weight ratio) so that it may be in agreement with the irreversible capacity of a negative electrode.

[0030] The cell of this invention is the most effective in the system which does not have a circuit for overdischarge prevention as a system of a cell, and can supply insurance, high capacity, and a cheap cell system.

[0031] With the system of the above-mentioned cell, all the devices carrying the circumference circuit for controlling a cell and a cell, a charge device, and its cell are packed.

[0032] About especially the raw material at the time of compounding the positive active material of this invention, a lithium carbonate, a lithium hydroxide, a lithium nitrate, lithium sulfate, and lithium oxide are desirable as lithium salt, and a lithium hydroxide and a lithium carbonate are desirable also in it. Moreover, as a source of aluminum, an aluminum hydroxide, an aluminium nitrate, an aluminum oxide, aluminum fluoride, an aluminum sulfate, etc. can be used. As a source of cobalt, basic cobalt carbonate, cobalt hydroxide, a cobalt nitrate, cobalt sulfate, cobalt oxide, fluoridation cobalt, etc. can be used. As ****, copper oxide, a copper sulfate, copper carbonate, copper acetate, oxalic acid copper, a copper chloride, copper sulfide, etc. can be used. As a source of zinc, a zinc oxide, zinc acetate, a zinc chloride, zinc fluoride, a zinc sulfate, zinc nitrate, zinc sulfide, etc. are mentioned. As magnesium salt, a

magnesium oxide, basic magnesium carbonate, a magnesium chloride, magnesium fluoride, a magnesium nitrate, magnesium sulfate, magnesium acetate, oxalic acid magnesium, sulfuration magnesium, a magnesium hydroxide, etc. are mentioned. As a calcium salt, a calcium oxide, a calcium chloride, a calcium carbonate, As a source of strontium, a calcium fluoride, a calcium nitrate, a calcium sulfate, calcium sulfide, a calcium hydroxide, etc. A strontium oxide, a strontium chloride, a strontium carbonate, a strontium oxalate, As a source of barium, strontium fluoride, strontium sulfate, a strontium nitrate, a strontium hydroxide, a strontium sulfide, etc. The barium oxide, barium chloride, a barium carbonate, barium fluoride, a barium oxalate, a barium nitrate, a barium sulfate, a barium sulfide, etc. can be used.

[0033] When the class of salt of the cobalt used as especially the compound of an alloying element and a parent and nickel is unified, it dissolves and an eutectic is carried out to cobalt or nickel, the engine performance with good collapsibility is obtained with uniform mixing on atomic level being possible. As a class of salt, a sulfate is the most desirable.

[0034] As a negative-electrode ingredient, a lithium is constituted using a dope and the ingredient which can be dedoped. A lithium as a dope and an ingredient which can be dedoped an alloy ingredient, pyrolytic carbon, and corks (pitch coke and needle coke --) graphite, such as petroleum coke, glassy carbon, and an organic high-molecular-compound baking object (phenol resin --) A lithium content transition-metals oxide or a transition-metals sulfide of polymers, such as carbon materials, such as what calcinated and carbonized furan resin etc. at suitable temperature, a carbon fiber, and activated carbon, polyacethylene, polypyrrole, and the poly acene, $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and TiS_2 grade etc. is mentioned.

[0035] When a carbon material with a large irreversible capacity in early charges and discharges, such as hard carbon, is used for a negative electrode, degradation by potential rise of a negative electrode occurs especially at the time of overdischarge. In such a case, if the addition of the second active material of a positive electrode of this invention is made [many], the irreversible capacity of a positive electrode can also become large, a potential rise of the above-mentioned negative electrode can be prevented, and overdischarge degradation can be improved.

[0036] The nonaqueous electrolyte used for this invention consists of a solvent and lithium salt which dissolves in the solvent. As a non-aqueous solvent, a well-known ingredient and a well-known additive can be used. The mixed stock of aliphatic series carboxylate, such as the mixed stock of annular carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), and vinylene carbonate (VC), and un-annular carbonate, such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and dipropyl carbonate (DPC), or annular carbonate and un-annular carbonate and methyl formate, methyl acetate, methyl propionate, and ethyl propionate, and annular are desirable especially.

[0037] As lithium salt of the nonaqueous electrolyte rechargeable battery used for this invention, each thing which is not limited but is usually used with the nonaqueous electrolyte rechargeable battery can use it especially by this invention. concrete -- LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)$ ($\text{C}_2\text{F}_5\text{SO}_2$), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ and $\text{LiN}(\text{CF}_3\text{SO}_2)(\text{C}_4\text{F}_9\text{SO}_2)$, and $\text{LiB}[\text{--C}_6\text{F}_3(\text{CF}_3)_2\text{--3 and 5}]$ -- the 4th grade can be used. Moreover, these lithium salt may mix two or more kinds, and may be used.

[0038] As an electrolyte of the nonaqueous electrolyte rechargeable battery used for this invention, each thing which is not limited but is usually used with the nonaqueous electrolyte rechargeable battery can use it especially by this invention. Moreover, effectiveness with the same said of mixing two or more kinds of these electrolytes can be acquired.

[0039] Moreover, the following is usable, although positive active material and a negative-electrode ingredient are kneaded with a binder and an electric conduction agent and are processed into a plate.

[0040] As a binder for negative electrodes used for this invention, you may be any of thermoplastics and thermosetting resin. These ingredients can be used as independent or mixture. Moreover, the more desirable ingredient in these ingredients is styrene butadiene rubber, polyvinylidene fluoride, an ethylene-acrylic-acid copolymer or the ion (Na^+) bridge formation object of said ingredient, an ethylene-methacrylic-acid copolymer or the ion (Na^+) bridge formation object of said ingredient, an

ethylene-methyl-acrylate copolymer or the ion (Na^+) bridge formation object of said ingredient, an ethylene-methyl-methacrylate copolymer, or the ion (Na^+) bridge formation object of said ingredient. [0041] If the electric conduction agent for negative electrodes used for this invention is an electronic conduction nature ingredient, it is good anything. Especially, an artificial graphite, acetylene black, and especially a carbon fiber are desirable. Although especially the addition of an electric conduction agent is not limited, its 1 - 50 % of the weight is desirable to a negative-electrode ingredient, and its 1 - 30 % of the weight is especially desirable. When negative-electrode ingredient itself has electronic conduction nature, electric conduction material may not be added.

[0042] If the charge collector for negative electrodes used for this invention is an electronic conductor which does not cause a chemical change in the constituted cell, this invention is the most effective to what carries out oxidizing melting with positive-electrode potential (about 3.5Vvs(es).Li/Li+) anything at the time of overdischarges, such as copper or a copper alloy, although it is good. It can oxidize and the front face of these ingredients can also be used. Moreover, it is desirable to attach irregularity to a current collection body surface by surface treatment. Although especially thickness is not limited, a 1-500-micrometer thing is used.

[0043] In the charge and discharge potential of the positive active material to be used, if the electric conduction agent for positive electrodes used by this invention is an electronic conduction nature ingredient which does not cause a chemical change, it is good anything. Especially, an artificial graphite and especially acetylene black are desirable. Although especially the addition of an electric conduction agent is not limited, its 1 - 50 % of the weight is desirable to positive active material, and its 1 - 30 % of the weight is especially desirable. In carbon or especially graphite, 2 - 15 % of the weight is desirable.

[0044] The binders for positive electrodes used for this invention may be any of thermoplastics and thermosetting resin. These ingredients can be used as independent or mixture. Moreover, the more desirable ingredients in these ingredients are polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE).

[0045] If the charge collector for positive electrodes used for this invention is an electronic conductor which does not cause a chemical change in the charge and discharge potential of the positive active material to be used, it is good anything. Especially, aluminum or an aluminium alloy is desirable. It can oxidize and the front face of these ingredients can also be used. Moreover, it is desirable to attach irregularity to a current collection body surface by surface treatment. Although especially thickness is not limited, a 1-500-micrometer thing is used.

[0046] an electrode -- a filler besides an electric conduction agent or a binder, a dispersant, an ion conductor, a pressure enhancement agent, and other various additives can be used for a mixture. although especially the addition of a filler is not limited -- an electrode -- 0 - 30 % of the weight is desirable to a mixture.

[0047] the configuration of the negative-electrode plate in this invention, and a positive-electrode plate - - at least -- a positive electrode -- a mixture -- the opposed face of a field -- a negative electrode -- a mixture -- it is desirable that the field exists.

[0048] As a separator used for this invention, it has big ion transmittance, and has a predetermined mechanical strength, and an insulating fine porosity thin film is used. Moreover, it is desirable to have the function to blockade a hole above constant temperature and to raise resistance. As for the aperture of a separator, it is desirable that it is the range which the forward negative-electrode ingredient from which it was desorbed from the electrode sheet, a binder, and an electric conduction agent do not penetrate, for example, what is 0.01-1 micrometer is desirable. A 10-300-micrometer thing can be used for the thickness of a separator. Moreover, although a void content is determined according to the permeability, the material, and film pressure of an electron or ion, it is desirable that it is generally 30 - 80%.

[0049] moreover, the thing which carried out absorption maintenance of the organic electrolytic solution constituted from lithium salt which dissolves in a solvent and its solvent by the polymer ingredient -- a positive electrode -- a mixture and a negative electrode -- it is also possible to constitute the cell which united with the positive electrode and the negative electrode the porous separator which consists of a

polymer which is included in a mixture and carries out absorption maintenance of the organic electrolytic solution further. As this polymer ingredient, be [what is necessary / just although the absorption maintenance of the organic electrolytic solution can be carried out], especially the copolymer of vinylidene fluoride and hexafluoropropylene is desirable.

[0050] The gestalt of concrete operation of this invention is explained below, referring to a drawing. The square shape nonaqueous electrolyte rechargeable battery (width of face of 34mm, height of 50mm) used for drawing 1 by this example is shown. Through a separator, a band-like positive-electrode plate and a negative-electrode plate are wound in the shape of a multiple-times swirl, and a group of electrode 1 is constituted so that more clearly than this drawing. The positive-electrode lead 2 made from aluminum and the negative-electrode lead 3 made from nickel are welded to the positive-electrode plate and the negative-electrode plate, respectively. The upper part of a group of electrode is equipped with the insulating ring made of polyethylene resin, and it holds in the cell case 4 made from aluminum. Spot welding of the other end of the positive-electrode lead 2 is carried out to the obturation plate 5 made from aluminum, and spot welding of the other end of the negative-electrode lead 3 is carried out to the lower part of the negative-electrode terminal 6 made from nickel in the core of the obturation plate 5. Laser welding of the opening perimeter and the obturation plate 5 of the cell case 4 is carried out, and the nonaqueous electrolyte of the specified quantity is poured in from an inlet 8. Finally, the plug made from aluminum is used, laser welding of the inlet 8 is carried out, and a cell is completed. Although here explained using the square shape cell, the invention in this application can apply the large-sized thing used for a coin mold, a carbon button mold, a sheet mold, a laminating mold, cylindrical, flat, a square shape, an electric vehicle, etc. to any configuration of a cell.

[0051] (Example 1) Empirical formula $\text{LiCo}_{0.9}\text{aluminum } 0.1\text{O}_2$ is used as the first active material of a positive electrode. This positive active material trickled the sodium hydroxide into the mixed water solution in which the cobalt sulfate of 0.9 mol/l and the aluminum sulfate of 0.1 mol/l were dissolved, and it compounded the precursor, carrying out [adjusted pH at that time so that it might be set to 13 from 10, and] continuation supply of each ingredient. As a result, $\text{OH}(\text{Co}_{0.9}\text{aluminum } 0.1)_2$ of a hydroxide was obtained. It ground, after the sum total mol [of the cobalt in a precursor and aluminum] mole ratio's having mixed the lithium carbonate with this precursor after that so that it might be set to $\text{Li}:(\text{Co}+\text{aluminum})=1:1$, and performing temporary baking at 600 degrees C, and after calcinating again and grinding and classifying at 900 degrees C, it considered as the first active material ingredient of a positive electrode of this invention. In addition, the air ambient atmosphere performed firing time respectively in 10 hours.

[0052] Empirical formula $\text{Li}_{0.85}\text{nickel } 0.15\text{CoO}_2$ is used as the second active material of a positive electrode. This positive active material trickled the sodium hydroxide into the mixed water solution in which the nickel sulfate of 0.85 mol/l and the cobalt sulfate of 0.15 mol/l were dissolved, and it compounded the precursor, carrying out [adjusted pH at that time so that it might be set to 13 from 10, and] continuation supply of each ingredient. As a result, $\text{OH}(\text{nickel } 0.85\text{Co } 0.15)_2$ of a hydroxide was obtained. It ground, after the lithium in the sum total mol of the nickel in a precursor and cobalt and a lithium hydroxide and the nickel in a precursor, and the mole ratio of cobalt having mixed the lithium hydroxide with this precursor after that so that it might be set to 1:0.85:0.15, and performing temporary baking at 600 degrees C, and after calcinating again and grinding and classifying at 800 degrees C, it considered as the second active material ingredient of a positive electrode of this invention. In addition, firing time performed baking under the oxygen ambient atmosphere respectively in 10 hours.

[0053] thus, obtained first active material LiCoO_2 positive electrode $\text{Co}_{0.9}\text{aluminum } 0.1\text{O}_2$ and a positive electrode second -- 70:30 came out of active material $\text{LiNi}_{0.85}\text{Co } 0.15\text{O}_2$ comparatively, and it mixed, and considered as total positive active material.

[0054] polyvinylidene fluoride becomes this total positive-active-material 100 weight section as electric conduction material, and becomes 5 weight sections as the acetylene black 3 weight section and a binder -- as -- N-methyl pyrrolidinone solution of polyvinylidene fluoride -- adjusting -- stirring mixing -- carrying out -- a paste-like positive electrode -- the mixture was obtained. next, aluminium foil with a thickness of 20 micrometers -- a charge collector -- carrying out -- the both sides -- said paste-like

positive electrode -- the mixture was applied, and it rolled out with the rolling roller after desiccation, it judged in the predetermined dimension, and considered as the positive-electrode plate.

[0055] Moreover, the negative electrode was produced as follows. first, after mixing the styrene / butadiene rubber 3 weight section of a binder with the scale-like graphite which ground and classified so that a mean diameter may be set to about 20 micrometers, a carboxymethyl cellulose becomes 1% to a graphite -- as -- a carboxymethyl-cellulose water solution -- adding -- stirring mixing -- carrying out -- a paste-like negative electrode -- it considered as the mixture. copper foil with a thickness of 15 micrometers -- a charge collector -- carrying out -- the both sides -- a paste-like negative electrode -- the mixture was applied, and it rolled out using the rolling roller after desiccation, it judged in the predetermined dimension, and considered as the negative-electrode plate.

[0056] And the seal plug was carried out after pouring this in the solvent which adjusted ethylene carbonate and ethyl methyl carbonate for the band-like positive electrode produced as mentioned above, the negative electrode, and the separator made of fine porosity polyethylene resin with a thickness of 25 micrometers to winding and nonaqueous electrolyte at a rate of 30:70 spirally using what dissolved LiPF₆ of 1.0 mol/l. Thus, the produced cell was used as the cell 1 of this invention.

[0057] (Example 2) Using OH(Co_{0.9}Cu_{0.1})₂ of the hydroxide compounded as a precursor, in the sum total mol of the cobalt and copper in a precursor, the lithium carbonate was mixed so that it might be set to Li:(Co+Cu)=1:1, and except having used the first active material of a positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 2 of this invention.

[0058] (Example 3) Using OH(Co_{0.9}Zn_{0.1})₂ of the hydroxide compounded as a precursor, in the sum total mole ratio of the cobalt in a precursor, and zinc, the lithium carbonate was mixed so that it might be set to Li:(Co+Zn)=1:1, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 3 of this invention.

[0059] (Example 4) Using OH(Co_{0.9}Mg_{0.1})₂ of the hydroxide compounded as a precursor, in the sum total mole ratio of the cobalt and magnesium in a precursor, the lithium carbonate was mixed so that it might be set to Li:(Co+Mg)=1:1, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 4 of this invention.

[0060] (Example 5) Using OH(Co_{0.9}calcium_{0.1})₂ of the hydroxide compounded as a precursor, in the sum total mole ratio of the cobalt in a precursor, and calcium, the lithium carbonate was mixed so that it might be set to Li:(Co+calcium)=1:1, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 5 of this invention.

[0061] (Example 6) Using OH(Co_{0.9}Ba_{0.1})₂ of the hydroxide compounded as a precursor, a lithium carbonate is set to the sum total mole ratio of the cobalt and barium in a precursor, and it is Li : (it mixed so that it might be set to Co+Ba=1:1, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 6 of this invention.)

[0062] (Example 7) Using OH(Co_{0.9}Sr_{0.1})₂ of the hydroxide compounded as a precursor, in the sum total mole ratio of the cobalt and strontium in a precursor, the lithium carbonate was mixed so that it might be set to Li:(Co+Sr)=1:1, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 7 of this invention.

[0063] (Example 8) As positive active material, an empirical formula (Li_{0.95}aluminum_{0.05})(Co_{0.9}aluminum_{0.1})₂ O₂ is used as the first active material. This positive active material trickled the sodium hydroxide into the mixed water solution in which the cobalt sulfate of 0.9 mol/l and the aluminum sulfate of 0.1 mol/l were dissolved, and it compounded the precursor, carrying out [adjusted pH at that time so that it might be set to 13 from 10, and] continuation supply of each ingredient. As a result, OH(Co_{0.9}aluminum_{0.1})₂ of a hydroxide was obtained. It ground, after the mole ratio of the

cobalt in a precursor, the lithium in the sum total mol of aluminum and a lithium carbonate, and the aluminum in an aluminum hydroxide having mixed the lithium carbonate and the aluminum hydroxide with this precursor after that so that it might be set to $:(\text{Co}+\text{aluminum}) \text{Li}:\text{aluminum}=1:0.95:0.05$, and performing temporary baking at 600 degrees C, and after calcinating again and grinding and classifying at 900 degrees C, it considered as the first active material ingredient of a positive electrode of this invention. In addition, the air ambient atmosphere performed firing time respectively in 10 hours.

[0064] Empirical formula $\text{Li}_{0.85}\text{nickel}_{0.15}\text{CoO}_2$ is used as the second active material of a positive electrode. This positive active material trickled the sodium hydroxide into the mixed water solution in which the nickel sulfate of 0.85 mol/l and the cobalt sulfate of 0.15 mol/l were dissolved, and it compounded the precursor, carrying out [adjusted pH at that time so that it might be set to 13 from 10, and] continuation supply of each ingredient. As a result, $\text{OH}(\text{nickel}_{0.85}\text{Co}_{0.15})_2$ of a hydroxide was obtained. It ground, after having mixed the lithium hydroxide with this precursor in the lithium in the sum total mol of the nickel in a precursor, and cobalt, and a lithium hydroxide and the nickel in a precursor, and the mole ratio of cobalt after that so that it might be set to $1:0.85:0.15$, and performing temporary baking in 600 degrees C, and after calcinating again and grinding and classifying at 800 degrees C, it considered as the first active material ingredient of a positive electrode of this invention. In addition, firing time performed baking under the oxygen ambient atmosphere respectively in 10 hours.

[0065] Thus, the first active material $(\text{Li}_{0.95}\text{aluminum}_{0.05}) (\text{Co}_{0.9}\text{aluminum}_{0.1}) \text{O}_2$ of a positive electrode and the second active material $(\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2)$ of a positive electrode which were obtained were mixed at a rate of 70:30, and it considered as total positive active material. Except having used the above-mentioned positive active material, the cell was produced like the example 1 and it considered as the cell 8 of this invention.

[0066] $\text{OH}(\text{Co}_{0.9}\text{Cu}_{0.1})_2$ of the hydroxide compounded as a precursor is used. (Example 9) A lithium carbonate and copper carbonate the mole ratio of the cobalt in a precursor, the lithium in a copper sum total mol and a lithium carbonate, and the copper in copper carbonate $:(\text{Co}+\text{Cu})$ It mixed so that it might be set to $\text{Li}:\text{Cu}=1:0.95:0.05$, and except having used the first active material of a positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 9 of this invention.

[0067] $\text{OH}(\text{Co}_{0.9}\text{Zn}_{0.1})_2$ of the hydroxide compounded as a precursor is used. (Example 10) A lithium carbonate and a zinc oxide A zincky cobalt [in a precursor], and sum total mol, It mixed so that it might be set to $:(\text{Co}+\text{Zn}) \text{Li}:\text{Zn}=1:0.95:0.05$, and except having used the positive electrode compounded under the same conditions as an example 1, the mole ratio of the lithium in a lithium carbonate and the zinc in a zinc oxide produced the cell like the example 1, and considered as the cell 10 of this invention.

[0068] $\text{OH}(\text{Co}_{0.9}\text{Mg}_{0.1})_2$ of the hydroxide compounded as a precursor is used. (Example 11) A lithium carbonate and basic magnesium carbonate The cobalt [in a precursor], and sum total mol of magnesium, The mole ratio of the lithium in a lithium carbonate and the magnesium in a magnesium carbonate $:(\text{Co}+\text{Mg})$ It mixed so that it might be set to $\text{Li}:\text{Mg}=1:0.95:0.05$, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 11 of this invention.

[0069] $\text{OH}(\text{Co}_{0.9}\text{calcium}_{0.1})_2$ of the hydroxide compounded as a precursor is used. (Example 12) A lithium carbonate and a calcium carbonate The cobalt [in a precursor], and sum total mol of calcium, The mole ratio of the lithium in a lithium carbonate and the calcium in a calcium carbonate $:(\text{Co}+\text{calcium})$ It mixed so that it might be set to $\text{Li}:\text{calcium}=1:0.95:0.05$, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 12 of this invention.

[0070] $\text{OH}(\text{Co}_{0.9}\text{Ba}_{0.1})_2$ of the hydroxide compounded as a precursor is used. (Example 13) A lithium carbonate and a barium carbonate The cobalt [in a precursor], and sum total mol of barium, The mole ratio of the lithium in a lithium carbonate and the barium in a barium carbonate $:(\text{Co}+\text{Ba})$ It mixed so that it might be set to $\text{Li}:\text{Ba}=1:0.95:0.05$, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 13 of this invention.

[0071] $\text{OH}(\text{Co}_{0.9}\text{Sr}_{0.1})_2$ of the hydroxide compounded as a precursor is used. (Example 14) A lithium carbonate and a strontium carbonate The cobalt [in a precursor], and sum total mol of strontium, The mole ratio of the lithium in a lithium carbonate and the strontium in a strontium carbonate : $(\text{Co}+\text{Sr})$ It mixed so that it might be set to $\text{Li}:\text{Sr}=1:0.95:0.05$, and except having used the positive electrode compounded under the same conditions as an example 1, the cell was produced like the example 1 and it considered as the cell 14 of this invention.

[0072] (Example 15) Except having used the second active material of a positive electrode which mixed with the lithium hydroxide $\text{OH}(\text{nickel}_{0.85}\text{Mn}_{0.15})_2$ of the hydroxide compounded as a precursor as the second active material of a positive electrode, and was compounded on the same conditions as an example 1, the cell was produced under the same conditions as an example 1, and it considered as the cell 15 of this invention.

[0073] (Example 16) Except having used the second active material of a positive electrode which mixed with the lithium hydroxide $\text{OH}(\text{nickel}_{0.85}\text{Cr}_{0.15})_2$ of the hydroxide compounded as a precursor as the second active material of a positive electrode, and was compounded on the same conditions as an example 1, the cell was produced under the same conditions as an example 1, and it considered as the cell 16 of this invention.

[0074] (Example 17) Except having used the second active material of a positive electrode which mixed with the lithium hydroxide $\text{OH}(\text{nickel}_{0.85}\text{Fe}_{0.15})_2$ of the hydroxide compounded as a precursor as the second active material of a positive electrode, and was compounded on the same conditions as an example 1, the cell was produced under the same conditions as an example 1, and it considered as the cell 17 of this invention.

[0075] (Example 18) Except having used the second active material of a positive electrode which mixed with the lithium hydroxide $\text{OH}(\text{nickel}_{0.85}\text{V}_{0.15})_2$ of the hydroxide compounded as a precursor as the second active material of a positive electrode, and was compounded on the same conditions as an example 1, the cell was produced under the same conditions as an example 1, and it considered as the cell 18 of this invention.

[0076] (Example 19) Except having used the second active material of a positive electrode which mixed with the lithium hydroxide $\text{OH}(\text{nickel}_{0.85}\text{aluminum}_{0.15})_2$ of the hydroxide compounded as a precursor as the second active material of a positive electrode, and was compounded on the same conditions as an example 1, the cell was produced under the same conditions as an example 1, and it considered as the cell 19 of this invention.

[0077] (Example 20) Except having used the second active material of a positive electrode which mixed with the lithium hydroxide $\text{OH}(\text{nickel}_{0.85}\text{Co}_{0.10}\text{aluminum}_{0.05})_2$ of the hydroxide compounded as a precursor as the second active material of a positive electrode, and was compounded on the same conditions as an example 1, the cell was produced under the same conditions as an example 1, and it considered as the cell 20 of this invention.

[0078] (Example 21) After kneading a graphite particle in the pitch component of a solution layer as a negative-electrode ingredient, using the very small carbon material of irreversible capacity calcinated at 1000 degrees C under the inert atmosphere, except having set the mixing ratio of the first active material of a positive electrode, and the second active material of a positive electrode to 97:3, the cell was produced under the same conditions as an example 1, and it considered as the cell 21 of this invention.

[0079] (Example 22) After kneading a graphite particle in the pitch component of a solution layer as a negative-electrode ingredient, using the very small carbon material of irreversible capacity calcinated at 1000 degrees C under the inert atmosphere, except having set the mixing ratio of the first active material of a positive electrode, and the second active material of a positive electrode to 95:5, the cell was produced under the same conditions as an example 1, and it considered as the cell 21 of this invention.

[0080] (Example 23) Using the very large hard carbon of irreversible capacity as a negative-electrode ingredient, except having set the mixing ratio of the first active material of a positive electrode, and the second active material of a positive electrode to 30:70, the cell was produced under the same conditions as an example 1, and it considered as the cell 23 of this invention.

[0081] (Example 24) Except having set the mixing ratio of the first active material of a positive

electrode, and the second active material of a positive electrode to 20:80 for the very large hard carbon of irreversible capacity, using a carbon material as a negative-electrode ingredient, the cell was produced under the same conditions as an example 1, and it considered as the cell 24 of this invention.

[0082] (Example 1 of a comparison) $\text{Co}(\text{OH})_2$ and the lithium carbonate of a hydroxide -- lithium: -- it mixed so that the mole ratio of cobalt might become equimolar, and LiCoO_2 compounded under the same conditions as the first active material of a positive electrode of an example 1 was used for the positive electrode, the above-mentioned cell was produced, and it considered as the cell 25 of a comparison of this invention.

[0083] (Example 2 of a comparison) nickel $(\text{OH})_2$ and the lithium hydroxide of a hydroxide -- lithium: - it mixed so that the mole ratio of nickel might become equimolar, and the above-mentioned cell was produced using LiNiO_2 positive electrode compounded under the same conditions as the second active material of a positive electrode of an example 1, and it considered as the cell 26 of a comparison of this invention.

[0084] (Example 3 of a comparison) $\text{OH}(\text{Co}_{0.85}\text{aluminum}_{0.15})_2$ and the lithium carbonate of a hydroxide which used as the precursor and were compounded were mixed so that the mole ratio of lithium:cobalt + aluminum might become equimolar, the above-mentioned cell was produced using the positive electrode compounded under the same conditions as an example 1, and it considered as the cell 27 of a comparison of this invention.

[0085] (Example 4 of a comparison) $\text{OH}(\text{nickel}_{0.85}\text{Co}_{0.15})_2$ and the lithium hydroxide of a hydroxide which used as the precursor and were compounded were mixed so that the mole ratio of lithium:nickel + cobalt might become equimolar, $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ compounded under the same conditions as the second active material of a positive electrode of an example 1 was used for the positive electrode, the above-mentioned cell was produced, and it considered as the cell 28 of a comparison of this invention.

[0086] It mixes so that the mole ratio of cobalt may become equimolar. (Example 5 of a comparison) $\text{Co}(\text{OH})_2$ and the lithium carbonate of a hydroxide -- lithium: -- It mixes so that the mole ratio of nickel + cobalt may become equimolar. the hydroxide and lithium hydroxide which consist of LiCoO_2 compounded under the same conditions as the first active material of a positive electrode of an example 1, and $\text{OH}(\text{nickel}_{0.85}\text{Co}_{0.15})_2$ compounded as a precursor -- lithium: -- The above-mentioned cell was produced using the positive electrode which mixed the positive electrode compounded under the same conditions as the second active material of a positive electrode of an example 1 at a rate of 30:70, and it considered as the cell 29 of a comparison of this invention.

[0087] In addition, although the different-species element introduced into the first active material of a positive electrode and each second active material of a positive electrode was made into one kind in this example, it checked separately that two or more sorts of different-species elements were introduced, and there was same effectiveness.

[0088] The charge-and-discharge cycle was performed for the cell of this invention created in examples 1-24 and the examples 1-5 of a comparison, and the comparative cell with the environmental temperature of 20 degrees C. Charge conditions made 2 hours constant-potential charge 600mA of maximum current and whose charge termination potential are 4.2V. It presupposed that discharge conditions are carried out by the current value of 600mA, and the constant current of discharge termination potential 3.0V, and they performed evaluation of initial capacity, and evaluation of a cycle property.

[0089] Moreover, after performing constant-potential charge 600mA of maximum current and whose charge termination potential are 4.2V at 20 degrees C about charge as evaluation of a low-temperature property for 2 hours, it carried out by the aftercurrent value of 600mA which left the cell at -20 degrees C for 6 hours, and the constant current of discharge termination potential 3.0V.

[0090] Moreover, after 20 degrees C estimated initial capacity as evaluation of a preservation property, after leaving the cell of a charge condition for 20 days at 60 degrees C, the same charge-and-discharge conditions performed the charge and discharge test at 20 degrees C again, and the recovery factor of capacity was measured.

[0091] Moreover, after 20 degrees C estimated initial capacity as evaluation of an overdischarge

recovery property, after leaving it for three weeks and making an overdischarge condition go through at 45 degrees C where resistance of 1kohm is connected to the cell of a discharge condition, the same charge-and-discharge conditions performed the charge and discharge test at 20 degrees C again, and the recovery factor of capacity was measured.

[0092] Moreover, as a safety test, the overcharge trial was continuously performed for the cell with the current value of 900mA from the charge condition, and the safety of a cell was evaluated.

[0093] A capacity maintenance factor [as opposed to / as opposed to / to (Table 1) / the positive-active-material presentation of the cell of an example and the example of a comparison / initial capacity, -20 degree-C discharge capacity, and the cell capacity of 1 cycle eye after 500 cycle progress to (Table 2)], the recovery property after overdischarge progress at 45 degrees C, and the abnormality heat rate in the overcharge trial (n= 20) by 900mA are shown. Abnormality generation of heat was considered as the case where it exceeds 120 degrees C which is the heat-resistant temperature of a separator here.

[0094]

[Table 1]

	正極活物質		第一：第二 混合比率
	第一活物質	第二活物質	
実施例1	$\text{LiCo}_{0.9}\text{Al}_{0.1}\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例2	$\text{LiCo}_{0.9}\text{Cu}_{0.1}\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例3	$\text{LiCo}_{0.9}\text{Zn}_{0.1}\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例4	$\text{LiCo}_{0.9}\text{Mg}_{0.1}\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例5	$\text{LiCo}_{0.9}\text{Ca}_{0.1}\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例6	$\text{LiCo}_{0.9}\text{Ba}_{0.1}\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例7	$\text{LiCo}_{0.9}\text{Sr}_{0.1}\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例8	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例9	$(\text{Li}_{0.95}\text{Cu}_{0.05})(\text{Co}_{0.9}\text{Cu}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例10	$(\text{Li}_{0.95}\text{Zn}_{0.05})(\text{Co}_{0.9}\text{Zn}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例11	$(\text{Li}_{0.95}\text{Mg}_{0.05})(\text{Co}_{0.9}\text{Mg}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例12	$(\text{Li}_{0.95}\text{Ca}_{0.05})(\text{Co}_{0.9}\text{Ca}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例13	$(\text{Li}_{0.95}\text{Ba}_{0.05})(\text{Co}_{0.9}\text{Ba}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例14	$(\text{Li}_{0.95}\text{Sr}_{0.05})(\text{Co}_{0.9}\text{Sr}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30
実施例15	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Mn}_{0.15}\text{O}_2$	70:30
実施例16	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Cr}_{0.15}\text{O}_2$	70:30
実施例17	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Fe}_{0.15}\text{O}_2$	70:30
実施例18	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{V}_{0.15}\text{O}_2$	70:30
実施例19	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Al}_{0.15}\text{O}_2$	70:30
実施例20	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Al}_{0.05}\text{O}_2$	70:30
実施例21	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	97:3
実施例22	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	95:5
実施例23	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	30:70
実施例24	$(\text{Li}_{0.95}\text{Al}_{0.05})(\text{Co}_{0.9}\text{Al}_{0.1})\text{O}_2$	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	20:80
比較例1	LiCoO_2		
比較例2	LiNiO_2		
比較例3	$\text{LiCo}_{0.85}\text{Al}_{0.15}\text{O}_2$		
比較例4	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$		
比較例5	LiCoO_2	$\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$	70:30

[0095]

[Table 2]

	初期容量 (mAh)	-20℃容量 (mAh)	サイクル維持 (%)	保存回復 (%)	過放電 回復 (%)	過充電 発熱
実施例1	661	341	82	91	97	0/20
実施例2	662	344	81	90	98	0/20
実施例3	660	340	83	92	97	0/20
実施例4	664	340	82	91	96	0/20
実施例5	662	345	82	91	98	0/20
実施例6	661	347	81	90	97	0/20
実施例7	663	346	80	92	98	0/20
実施例8	650	330	81	90	98	0/20
実施例9	652	325	82	91	97	0/20
実施例10	648	340	81	93	98	0/20
実施例11	653	328	85	92	98	0/20
実施例12	657	331	84	90	99	0/20
実施例13	649	324	80	92	98	0/20
実施例14	647	319	83	90	98	0/20
実施例15	655	324	83	90	97	0/20
実施例16	657	329	82	91	97	0/20
実施例17	653	345	84	91	98	0/20
実施例18	654	341	81	92	98	0/20
実施例19	652	328	80	92	98	0/20
実施例20	653	333	80	92	98	0/20
実施例21	649	325	82	91	88	0/20
実施例22	635	325	82	91	97	0/20
実施例23	670	342	83	90	98	0/20
実施例24	678	305	82	91	97	0/20
比較例1	621	367	78	91	62	17/20
比較例2	688	201	51	88	57	2/20
比較例3	615	358	81	65	54	0/20
比較例4	681	185	80	85	56	1/20
比較例5	655	318	82	87	85	17/20

[0096] The cell of the example of a comparison is first described from the result of (Table 2). By the cell 25 which used only LiCoO₂ for the positive active material of the example 1 of a comparison, although the low-temperature property and the cycle property were excellent, its discharge capacity was small, and the problem was in the safety of overcharge, and the recovery property after overdischarge. Moreover, when the cell after overdischarge was disassembled and analyzed, it turned out that the copper core material which the copper sludge was observed on the negative-electrode front face, and dissolved at the time of overdischarge is degrading the cell.

[0097] On the other hand, although a large discharge capacity was obtained by the cell 26 which used only LiNiO₂ for the positive active material of the example 2 of a comparison, the problem was in the low-temperature property, the cycle property, and the recovery property after overdischarge. Moreover, although the degradation factor was not observed by especially the negative electrode when the cell after

overdischarge was disassembled and analyzed, the crystal structure of a positive electrode was destroyed. It was thought that the potential of a positive electrode descended and reduction decomposition was carried out from this at the time of overdischarge since a cell was positive-electrode capacity regulation.

[0098] Next, there is a problem that the recoverability of that an early discharge capacity is low and overdischarge is bad, and the cell 27 only using $\text{LiCo}_{0.85}\text{Al}_{0.15}\text{O}_2$ which added aluminum to the positive active material of the example 3 of a comparison LiCoO_2 is not enough as a cell, although effectiveness remarkable at the safety at the time of overcharge was acquired.

[0099] Although the cycle property has improved by the cell 28 which used $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ of the example 4 of a comparison for the positive electrode as a result of adding Co, a technical problem remains in a low-temperature property and the recovery property after overdischarge.

[0100] Although cell properties, such as discharge capacity and a recovery property after overdischarge, improve by the cell 29 which used LiCoO_2 of the example 5 of a comparison, and the mixture of $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ for the positive electrode, the safety at the time of overcharge is not securable.

[0101] Next, the cell of the example of the invention in this application is described. Although the cell of examples 8-15 had a small discharge capacity a little compared with the cell of examples 1-7 and the effect to which the different-species element went into the lithium layer was accepted, it was the capacity which is equal to use enough. And when a different-species element went into a lithium layer, the temperature rise in the time of a overcharge trial was small compared with the cell of examples 1-7, and it turned out that safety improves more. Moreover, the mixed ratio of the second positive active material brought especially the result of having excelled with sufficient balance of various properties, as an amount of mixing at the time of 5 - 70%, although the remarkable improvement was accepted by mixing from the result of examples 21-24 and the examples 3 and 4 of a comparison.

[0102] It turned out that high safety can be maintained at the time of overcharge since the cell using the positive active material in this invention has a large discharge capacity, a low-temperature property, a cycle property, and the recovery property after overdischarge are also good and the thermal stability in a overcharge condition is also high, and it excels in the dependability under the abnormality environment of a cell.

[0103]

[Effect of the Invention] it explained above -- as -- as the first active material of a positive electrode -- $\text{Li}_x\text{Co}_y\text{M}_w\text{O}_z$ ($1.10 \geq x \geq 0.9$, $0.98 \geq y \geq 0.85$, $0.02 \leq w \leq 0.15$, and $z = 1.8-2.2$), At least one or more kinds of elements chosen from aluminum, Cu, Zn, Mg, calcium, Ba, and Sr, It is $\text{LiANiBM}'\text{COD}$ (it Co(es) $1.02 \geq A \geq 0.3$, $0.98 \geq B \geq 0.5$, $0.02 \leq C \leq 0.5$, $D = 1.8-2.2$, and M') as the second active material of a positive electrode. By using the nonaqueous electrolyte rechargeable battery which consists of a positive electrode which mixed at least one or more kinds of elements chosen from Mn, Cr, Fe, V, and aluminum, discharge capacity is large, a low-temperature property, a cycle property, and an overdischarge-proof property are good, and the cell excellent in the safety at the time of overcharge can be offered.

[Translation done.]